THE BEHAVIOR OF THE SOLID STATE SULFIDE ELECTRODE IN LIME-SULFIDE SOLUTIONS*

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ABSTRACT

The potential of the solid state silver-silver sulfide electrode in pure sodium sulfide solutions appears to vary linearly with the logarithm of the concentration of the sulfide over a considerable range. The same concentrations of sulfide in the presence of lime produce a nonlinear response. Studies of carefully analyzed mixtures of sodium sulfide and sodium sulfhydrate alone and in the presence of lime indicated that this difference in behavior was due to a pH effect. This occurs because the second dissociation constant of hydrogen sulfide, which controls the relationship between the concentrations of the sulfide and hydrosulfide ions in solution, involves the hydrogen ion concentration. Studies of the effect of this equilibrium constant upon the potential of the silver-silver sulfide electrode indicate that the electrode responds only to the sulfide ion and this response is linear. Two plots are presented by which the sulfide and sulfhydrate ion concentrations can be determined individually if the potential of the silver-silver sulfide electrode and the pH are known. Improved accuracy can be obtained if the measurements can be made under an inert atmosphere.

INTRODUCTION

The theory describing the relationship between the potential developed at a metallic electrode and the concentration of the ions of the same metal in the solution has been known for many years and adequate treatments of the thermodynamic aspects are presented by Lingane (1), MacInnes (2), and Kolthoff and Furman (3). Improvements in electrodes and measuring devices have made some of these electrodes promising for use in monitoring and process control applications. The authors (4) have recently shown that the potential of the silver billet electrode, when plated with sulfide ions, is a linear function of the logarithm of the concentration of sodium sulfide in pure sodium sulfide solutions,

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and concluded that the electrode might, therefore, provide a simple means of determining and controlling the strength of sulfides in an unhairing bath.

However, application of the electrode to sodium sulfide solutions containing excess lime produced a nonlinear relationship. The potentials produced by the lower concentrations were higher than expected, while the potentials produced by solutions of higher concentrations were quite close to the expected value. A private communication from Malcolm Battles (5), who had tried the Orion‡ liquid membrane sulfide electrode, indicated that they experienced a variation of values with the pH of the solution. We, therefore, attempted to test the pH dependence of the solid state silver-silver sulfide electrode.

Mixed solutions made from carefully analyzed sodium sulfide and sodium sulfhydrate solutions were prepared so as to have constant levels of sulfur content but different pH values. The potentials of the electrodes and pH of the solutions were compared with the amounts of sulfide and sulfhydrate added to determine the nature of the pH effect.

This analysis indicated a possible effect of atmospheric oxygen and another set of experiments was made under a nitrogen atmosphere.

EXPERIMENTAL

A Beckman silver billet electrode was plated with silver sulfide by immersing in a one percent sodium sulfide solution and applying alternately for 20-second intervals 1.5 volts of positive or negative potential. The final treatment should be at a positive potential. A strip of silver foil acted as the second electrode for this plating. This silver sulfide plating is quite durable and can be used for many months without replating.

For the sulfide measurements the silver-silver sulfide electrode and the reference electrode were connected to a Beckman research pH meter and the potential was displayed on a Moseley 7100B strip chart recorder connected to the recorder output of the meter. The reference electrode was either the normal calomel electrode or a mercurous sulfate electrode. The mercurous sulfate electrode produces an electrode potential about 400 millivolts more negative than the calomel reference electrode and can be used where contamination with chloride ions must be avoided. The presence of small concentrations of chloride ion does not affect the potential of the silver-silver sulfide electrode.

The pH of the solutions was measured with a Beckman E2 high pH glass electrode with a calomel reference electrode attached to a Beckman Electroscan 30 which has an integral recording system.

Approximately five percent solutions of sodium sulfide and sodium sulfhydrate were prepared from reagent grade chemicals and analyzed for their sulfide

‡Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

content by either the ALCA-F51 method or The Society of Leathers Trades' Chemists Method SLM4/2 for sulfides in alkaline liquors. The latter method was more rapid and convenient.

These stock solutions were remade frequently to assure freedom from build up of oxidation products and were reanalyzed every third day to correct for the slight decrease in concentration with time due to oxidation. Calculated volumes of the stock solutions were taken to make solutions containing definite levels of total sulfides and definite proportions of sulfide to sulfhydrate. Analytical grade calcium hydroxide powder was added to some of the solutions. The amount varied from one to three grams per 75 ml. of solution and in all cases was above the amount necessary to produce a saturated solution.

After the effect of pH had been determined, a series of solutions was made from arbitrary volumes of the sulfide and sulfhydrate solutions and the total concentration of sulfides was determined directly on the solution after the electrode measurement.

The electrodes were suspended from electrode holders in a 150 ml. beaker set on a constant temperature plate (25°C.) over a magnetic stirrer. Usually 75 ml. of solution was used. The solution was stirred until the electrode potential or the pH reached the equilibrium value. The time to attain equilibration varied considerably from sample to sample and generally took about 15 minutes for the sulfide electrode and five minutes for the pH electrode. The pH meter was calibrated with a standard 12.45 pH buffer both before and after each determination.

Some of the later experiments were carried out with a rubber diaphragm covering the beaker to keep out the oxygen and a nitrogen inlet tube inserted into the solution so that the solution could be purged of oxygen. Nitrogen was bubbled through these solutions continuously while the measurement was being made.

RESULTS AND DISCUSSION

The substitution of the equivalent of the silver ion concentration obtained from the silver sulfide solubility product equation into the electrode potential gives Equation 1, which indicates that the electrode potential should be a straight

$$E_s = E^o{}_s - \frac{RT}{2F} \log (S^=) \qquad 1$$

line function of the logarithm of the sulfide ion concentration. Data obtained for a series of straight sodium sulfide concentrations produced the straight line shown in Figure 1. This line, although comparatively straight at the high concentrations, has a slight curve for the lower concentrations. When lime was added to each of the solutions the electrode potentials depicted by the solid circles in Figure 1 were obtained. The upper portion of the curve is a straight line

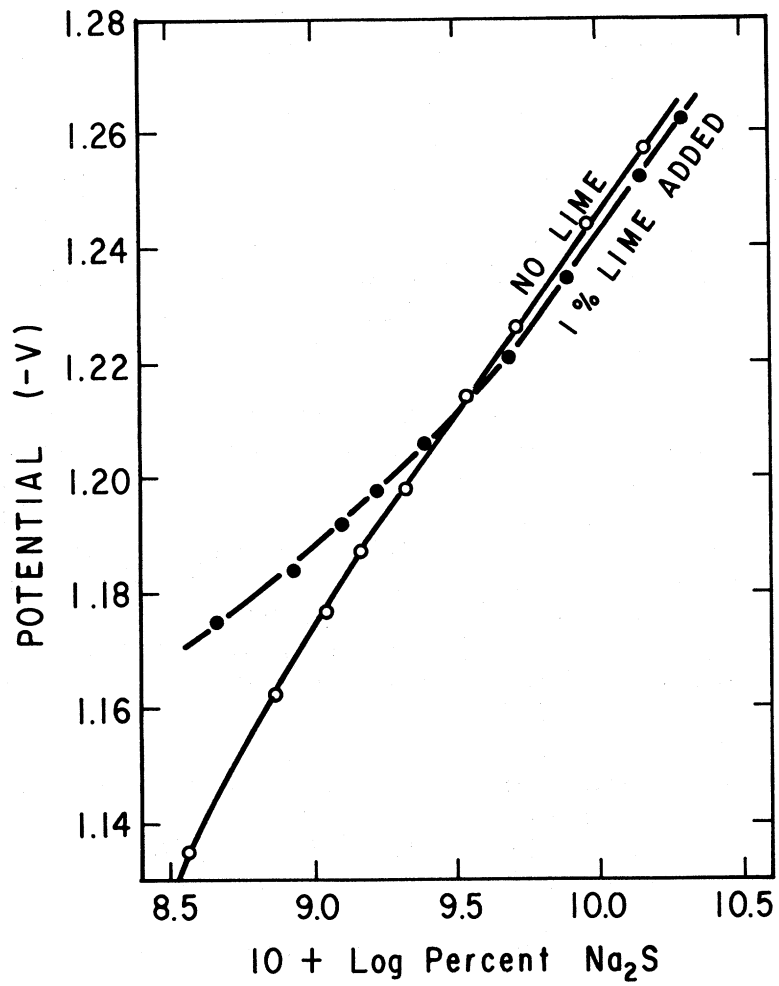

FIGURE 1.—Electrode potential in sodium sulfide solutions.

parallel to and only slightly removed from the curve obtained without lime. The lower portion curves in the opposite direction from the curve without lime.

Since Battles (5) has reported finding a pH dependence of the Orion liquid membrane sulfide electrode, a series of mixtures of sodium sulfide and sodium sulfhydrate was made to contain definite amounts of total sulfides and various ratios of sulfide to sulfhydrate ions. The results of these studies are shown in Figure 2, where the potential is plotted against the pH of the solution. The data for each fixed concentration falls on a straight line roughly parallel to the straight lines formed at other concentrations. This truly reflects a pH effect on

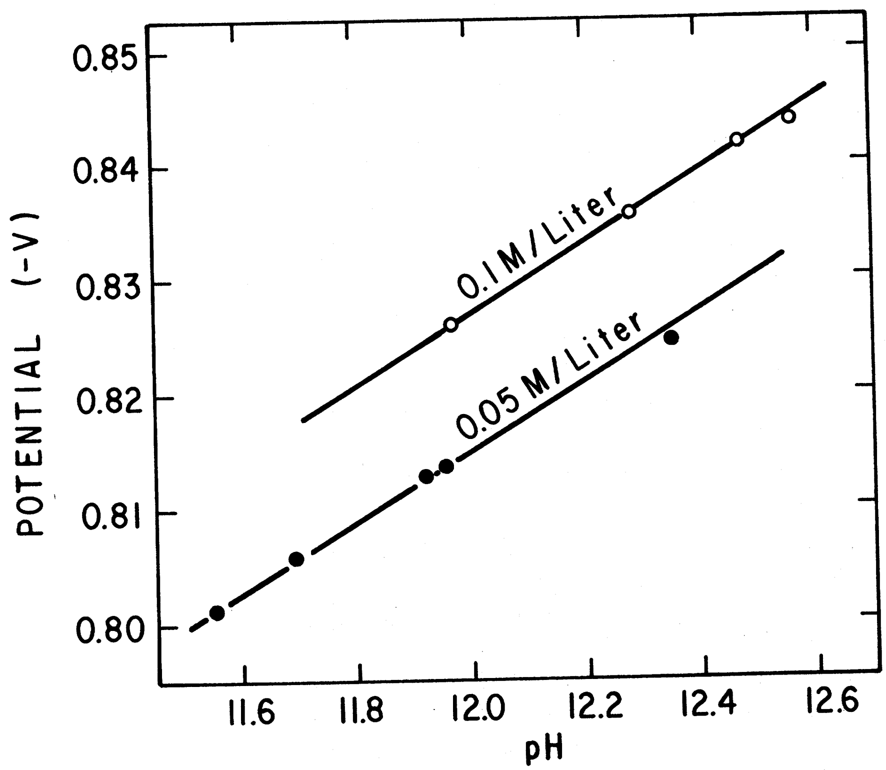

FIGURE 2.—Electrode potential as a function of pH at fixed concentrations of total sulfides.

the potential of the electrode. One possibility for a pH effect is the divalent nature of the sulfide ion. Equation 2 shows the equilibrium for the second ioniza-

$$\frac{(S^{=})(H^{+})}{(HS^{-})} = K_2 \qquad 2$$

tion constant. This equation can be rearranged and converted to obtain an equivalent of log $(S^{=})$ as shown in Equation 3.

$$\log (S^{=}) = -\log (H^{+}) + \log (HS^{-}) + \log K_2 \qquad 3$$

If one applies the definitions of pH and pK, one will obtain Equation 4, and

$$\log (S^{=}) = pH + \log (HS^{-}) - pK_2 \qquad 4$$

the equation for the potential of the solid state sulfide electrode can then be written as in Equation 5. As a result of this the electrode potential should give

$$E_S = E^{o}_{HS} - \frac{RT}{2F} [pH + \log (HS^{-})] \qquad 5$$

a straight line relationship if plotted against the sum of the pH and the log of the sulfhydrate ion concentration. At this point one must remember that the concentration of the sulfide or sulfhydrate ion to be used in the equations is the actual concentration or activity of the sulfide or sulfhydrate ion present and not the amount weighed out or added. Over the years there has been considerable controversy (6) concerning the second ionization constant of hydrogen sulfide but recently almost identical values have been given by Cloke (7) and Ste-Marie, Torma, and Gübeli (8). The pK_2 value of 13.48 at 25°C. given in the latter paper will be used for our calculations. Equation 4 shows that the logarithm of the ratio of the concentration of the sulfide ion to the concentration of the sulfhydrate ion depends only upon the pH and the value of pK_2. Since pK_2 is a constant at a given temperature, the ratio of the two ion concentrations varies only with the pH of the solution. Therefore, if the pH and the total sulfide concentration are known, the concentration of both the sulfide and sulfhydrate ions can be calculated.

When these calculations were made and the data plotted according to Equation 5, the lines shown in Figure 3 were obtained. The open circles represent sulfide solutions without lime present, while the closed circles and triangles represent sulfide solutions containing 1.3 and four percent of lime slurry. Here again the lime solutions have a slightly different trend than the nonlime solutions. There does not appear to be any difference between the two levels of lime. It is obvious that the data are a reasonable fit to the straight line. This would indicate that the only pH effect is that due to the second ionization constant of hydrogen sulfide and, therefore, the electrode is responding only to the sulfide ion. If the pH is known, then this curve can be used to determine the sulfhydrate ion concentration, and a plot of the potential against the sulfide ion concentration could give the actual sulfide ion concentration.

Windus and Showell (9) have recently discussed the mechanism of unhairing and concluded that the strong nucleophilic character of the sulfide ion was chiefly responsible for the unhairing activity in lime-sulfide unhairing systems. Therefore, the solid state silver-silver sulfide electrode which responds only to the sulfide ion content of the solution should be capable of measuring the unhairing potential of a lime-sulfide unhairing system.

It was noted that during the experiments required to produce the data for Figure 3, the electrode potential seemed to have a slight dependence upon the depth of immersion of the electrodes in the solution. We had also determined earlier that unstirred solutions gave a different potential than stirred solutions, and since the stirred solutions came to equilibrium more rapidly, all the solutions reported upon have been stirred. Since the sensing end of the electrode was completely immersed and the solutions were stirred it appeared that the variations of potential might be due to absorption of atmospheric oxygen by the solution,

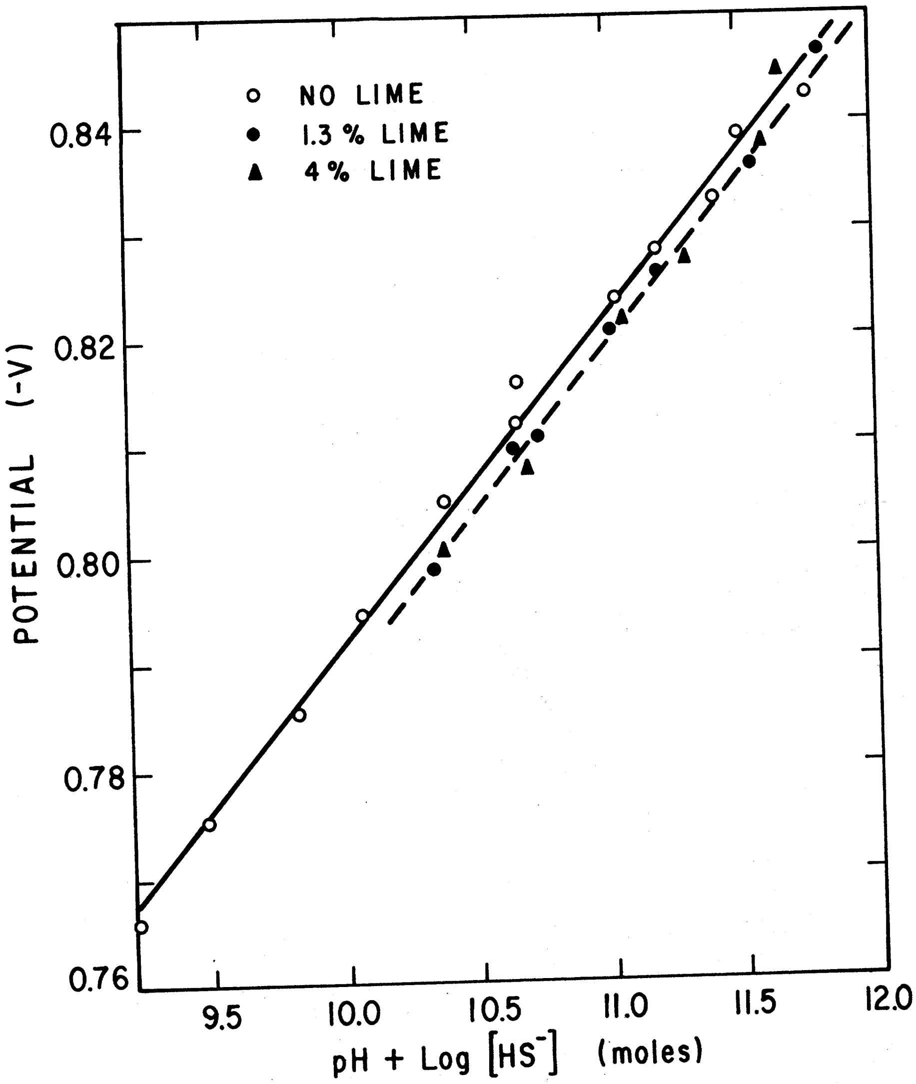

FIGURE 3.—Electrode potential as a function of pH and sulfhydrate concentration.

the depth of immersion controlling the amount of oxygen diffusing to the electrode.

An additional set of experiments was performed in which the measurements were done in a nitrogen atmosphere. Under these conditions neither stirring nor depth of immersion had an effect on the potential of the electrode. The results are given in Figure 4, where the potential is plotted as a function of sulfide ion concentration. The data fit the curve to a better degree than previously, but still contain a few points of relatively high error. Since only the total sulfide concen-

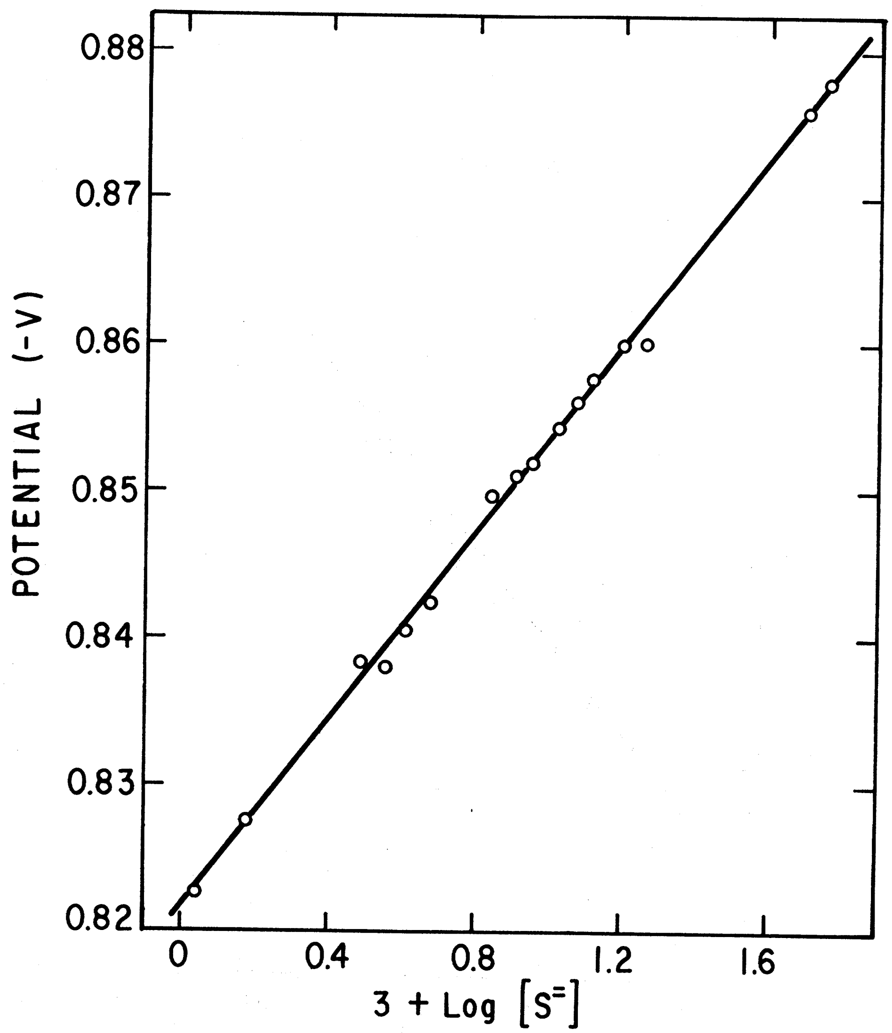

FIGURE 4.—Electrode potential under a nitrogen atmosphere as a function of sulfide ion concentration.

tration is known with certainty, the accuracy of the electrode in predicting the sulfide concentration can be judged only by summing up the sulfide ion concentration given by a plot similar to Figure 4 and the sulfhydrate ion concentration given by a plot similar to Figure 3. This was done for the data obtained under a nitrogen atmosphere and shown in Figure 4. The differences between the determined concentration and the sum of the sulfide and sulfhydrate ion concentrations given by the electrode are expressed as a percent of the analyzed value in Table I. It can be seen that three quarters of the observations are within five percent of the analytical value. The few values over five percent are probably due to a combination of inaccurate readings for both the sulfide and pH glass electrodes and a variation of the temperature of the solution. Since the concentration effect is on a logarithmic scale, small errors in the readings can produce large effects in the total result. Occasionally both sulfide and pH electrodes behave sluggishly and it is possible that at these times inaccurate readings are made.

TABLE I

DIFFERENCES BETWEEN CHEMICAL AND ELECTRODE ANALYSIS FOR SAMPLES IN A NITROGEN ATMOSPHERE

Electrode Data					Chemical Data	
Potential (—mv)	pH	Sulfide (M/L x 10^4)	Sulfhydrate (M/L x 10^4)	Total Sulfides (M/L x 10^4)	Total Sulfides (M/L x 10^4)	Difference (%)
824	12.50	12	105	117	114	2.6
828	12.48	15	141	156	164	4.9
832	12.31	21	295	316	286	10.5
838	12.58	32	245	277	326	15.0
838	12.58	32	245	277	277	0.0
841	12.59	38	302	340	369	7.8
843	12.54	44	380	424	464	8.6
848	12.56	64	524	588	572	2.8
849	12.66	74	478	552	529	4.3
851	12.66	81	524	605	612	1.1
852	12.63	87	602	689	702	1.8
855	12.63	105	741	846	860	1.6
856	12.75	120	631	751	745	0.4
858	12.73	132	758	890	909	2.1
858	12.75	132	708	840	845	0.6
859	12.80	151	676	827	960	13.8
860	12.71	157	921	1069	1124	4.9
860	12.72	157	891	1048	1061	1.2
876	13.03	501	1445	1946	1922	1.2
878	13.01	575	1736	2311	2303	0.3

CONCLUSIONS

The solid state silver-silver sulfide electrode produces a potential proportional only to the logarithm of the sulfide ion concentration and is not affected by the sulfhydrate ion present.

The ratio of sulfide ion to sulfhydrate ion concentrations depends upon the pH of the solution and, therefore, the electrode appears to be sensitive to pH when the potential is compared with the logarithm of the total combined sulfide concentrations or of the added sulfide concentration.

The solid state silver-silver sulfide electrode is sensitive to atmospheric oxygen and, therefore, it can be used only under controlled conditions.

Since the rate of unhairing is dependent upon the concentration of sulfide ion in solution, the solid state silver-silver sulfide electrode which responds only to sulfide ion could provide a measure of the unhairing ability of a lime sulfide solution and, therefore, could be used to control the unhairing procedure.

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DISCUSSION

MR. GROTA: Thank you, Dr. Mellon. The discussion leader for this paper will be Malcolm Battles of the A. C. Lawrence Leather Company.

MR. BATTLES: Sulfide unhairing systems play a large role in the preparation of hides and skins for tanning. They also contribute greatly to the waste disposal problems of tanneries. Dr. Mellon, do you think that the sulfide electrodes will find an application in the tannery?

DR. MELLON: Our study has shown that the sulfide electrode responds only to the concentration of the doubly charged sulfide ion, and since the ratio of sulfide ion to sulfhydrate ion or total sulfides depends upon the pH of the solution, it cannot be used to measure total sulfides present unless the pH is known. Below pH 11.5 the fraction of total sulfides present as sulfide ion is too small to enable the calculation of total sulfides from the electrode potential. Therefore, the electrode would be of little value for continuous monitoring of tannery effluents.

Theory indicates that only the sulfide ion is active in unhairing. Therefore, the electrode might be used to monitor unhairing baths. One major obstacle, however, is the oxygen sensitivity of the electrode. We hope to make some tannery trials of the electrode to test this theory.

MR. BATTLES: Since there are no comments from the floor, I wish to thank Ed for an interesting presentation.